

Two rubber balloons: Phase diagram of air transfer

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Two identical rubber balloons are partially inflated with air (to different extent) and connected by a hose with a valve. It is found that depending on initial balloon volumes, when the valve is opened the air will flow either from the larger (fuller) balloon to the smaller (emptier) balloon, or from the smaller balloon to the larger one. The phenomenon is explained in terms of the nonideal rubber elasticity of balloons. The full phase diagram for the air flow dynamics is constructed.

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I. INTRODUCTION

Consider two identical rubber balloons, the same ones as used at children's parties, filled with air and connected by a hose with a valve. For simplicity, we shall approximate the balloons by spheres. Suppose that the larger balloon, the one that has been inflated more, has radius R^b and contains n_b moles of air, while the smaller one has radius R^s and contains n_s moles of air. When the valve is opened which balloon is going to grow and which will shrink? It seems almost obvious that the larger balloon should shrink, while the smaller one should grow. This, however, is not what is often found. For some balloon sizes the air flows from the larger balloon to the smaller one, but for other sizes the direction of the air flow is reversed. What can explain this seemingly counterintuitive behavior?

II. THERMODYNAMICS

When the valve of the hose connecting the two balloons is opened, the direction of air flow is determined by the two laws of thermodynamics [1]. Suppose that $dn = -dn_b = dn_s$ moles of air are transferred from the bigger balloon to the smaller one. The work needed to accomplish this is determined by the first law of thermodynamics,

$$dW = TdS_0 + \sum_{i=s,b} (dE_i + dE_i^r + P_0 dV_i), \quad (1)$$

where S_0 , P_0 , and T are the environment entropy, pressure, and temperature; E_i , P_i , and V_i are the internal energy, pressure, and volume of the gas inside the two balloons $i=b,s$; and dE_i^r is the internal energy of the balloon rubber membranes. The second law of thermodynamics requires that

$$dS_0 + dS_b + dS_s + dS_b^r + dS_s^r \geq 0, \quad (2)$$

where S_i and S_i^r are the entropy of gas and of the rubber membrane of balloon i .

Since the transfer of dn moles of gas between the two balloons with finite pressure difference is an irreversible process, the total entropy of the universe will increase. It follows

that the work necessary for the transfer is bounded from below by

$$dW > \sum_{i=s,b} (dE_i + dE_i^r - TdS_i - TdS_i^r + P_0 dV_i). \quad (3)$$

From thermodynamics

$$dE_i = TdS_i - P_i dV_i + \mu_i dn_i \quad (4)$$

and

$$dE_i^r = TdS_i^r - P_i dV_i^r + \sigma_i dA_i, \quad (5)$$

where V_i^r is the volume of rubber, σ_i is the surface tension, A_i is the surface area, and μ_i is the chemical potential of gas inside the balloon i .

As a leading order approximation we can consider rubber to be incompressible, so that $dV_i^r = 0$. Substituting Eqs. (4) and (5) into Eq. (3), we obtain

$$dW > \sum_{i=s,b} [(P_0 - P_i)dV_i + \sigma_i dA_i + \mu_i dn_i]. \quad (6)$$

For a spherical balloon, the variations in the volume and in the surface area are related by

$$\frac{dV_i}{dA_i} = \frac{R_i}{2}, \quad (7)$$

while the difference between the internal and the external pressures is governed by the law of Laplace [1],

$$P_i - P_0 = \frac{2\sigma}{R_i}. \quad (8)$$

Substituting Eqs. (7) and (8) into Eq. (6), the amount of work necessary to accomplish the transfer of air is

$$dW > (\mu_s - \mu_b)dn. \quad (9)$$

For a gas at fixed temperature, the Gibbs-Duhem equation [2] is

$$-V_i dP_i + n_i d\mu_i = 0, \quad (10)$$

so that

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$$\left. \frac{\partial \mu_i}{\partial P_i} \right|_T = \frac{V_i}{n_i}. \quad (11)$$

Using the ideal gas equation of state and integrating, the chemical potential inside each balloon is found to be

$$\mu_i = \mu_0 + RT \ln\left(\frac{P_i}{P_0}\right), \quad (12)$$

where μ_0 is the reference chemical potential at atmospheric pressure. Inserting Eq. (12) into Eq. (9), the amount of work necessary to transfer dn moles of gas from the larger balloon to the smaller one is

$$dW > RT \ln\left(\frac{P_s}{P_b}\right) dn. \quad (13)$$

Transfer of gas will occur spontaneously if it does not require any external work, $dW=0$. For the specific case of two interconnected balloons this will be the case if the flow of air is from the balloon with high internal pressure to the one with low internal pressure. Furthermore, since the thermodynamics requires that $\partial\mu/\partial P > 0$, see Eq. (11), this conclusion holds for nonideal gases as well.

Although the calculation was performed for spherical balloons, it is evident that the conclusion concerning the direction of air flow, Eqs. (9) and (13), does not depend on the specific balloon shape. On the other hand, if the same balloons are filled with a heavy gas and are placed at different heights in the gravitational field, the flow of air will no longer be governed simply by the difference in internal pressure between the two balloons. Nevertheless, while Eq. (13) will lose its validity, Eq. (9) will remain correct; however, the chemical potential of gas will have to include a gravitational contribution as well.

III. RUBBER ELASTICITY

As air enters into the balloon, its rubber membrane stretches and becomes tense. The Helmholtz free energy of a rubber sheet is

$$F = E - TS. \quad (14)$$

If the sheet is subjected to a stress σ , its internal energy E will vary in accordance with Eq. (5), and its Helmholtz free energy as

$$dF = dE - TdS - SdT = -PdV - SdT + \sigma dA. \quad (15)$$

The surface tension of the sheet is then

$$\sigma = \left. \frac{\partial F}{\partial A} \right|_{V,T} = \left. \frac{\partial E}{\partial A} \right|_{V,T} - T \left. \frac{\partial S}{\partial A} \right|_{V,T}. \quad (16)$$

It is an experimental fact [3] that up to fairly large extensions the internal energy of a rubber sheet is independent of its area,

$$\left. \frac{\partial E}{\partial A} \right|_{V,T} = 0. \quad (17)$$

This equation should be compared to a similar equation for the ideal gas—the internal energy of an ideal gas is independent of the volume that it occupies. Clearly, this is not correct for real gases, but serves as a very good approximation for a gas at low density. Similarly, Eq. (17) holds only for “ideal” rubber.

The Flory theory [3] allows us to calculate the change in entropy of an elastic object during a deformation. Suppose that the rubber sheet has dimensions L_x , L_y , and L_z and that after the deformation the new dimensions are $\lambda_x L_x$, $\lambda_y L_y$, and $\lambda_z L_z$, then

$$\Delta S = -k[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 - \ln(\lambda_x \lambda_y \lambda_z)], \quad (18)$$

where k is a constant related to the number of chains and the topological structure of the polymer network. If rubber is subjected to a not very high stress it is reasonable to assume that it is incompressible, so that $\lambda_x \lambda_y \lambda_z = 1$. This means that for a uniform isotropic stress in the x - y plane, $\lambda_x = \lambda_y = \lambda$ and $\lambda_z = 1/\lambda^2$. Equation (18) then simplifies to

$$\Delta S = -k \left[\frac{2A}{A_0} + \frac{A_0^2}{A^2} - 3 \right], \quad (19)$$

where A_0 is the surface area prior to the deformation and A is the final surface area. It is important to note that a deformation of an elastic body results in a decrease of its entropy. Microscopically, this is a consequence of the reduction of the conformational volume accessible to a stretched polymer. Substituting Eq. (19) into Eq. (16), the surface tension of a rubber sheet is

$$\sigma = \kappa \left[1 - \frac{A_0^3}{A^3} \right], \quad (20)$$

where $\kappa = 2kT/A_0$.

We expect Eq. (20) to work reasonably well up to extensions on the order of 100%. If the balloon is inflated beyond this “ideal” limit, deviations are to be expected. In general then, the stress-strain relation for a rubber balloon of radius R can be written as

$$\sigma(R, R_0) \approx \kappa \left(1 - \frac{R_0^6}{R^6} \right) f\left(\frac{R}{R^*}\right), \quad (21)$$

where R_0 is the balloon radius prior to inflation, and the scaling function $f(x)$ governs the crossover from the ideal rubber regime to the nonideal one. The scale R^* specifies the balloon size at which its rubber starts to behave nonideally. Here we use the simplest form of the crossover function,

$$f(x) = \begin{cases} 1 & \text{for } 0 \leq x \leq 1 \\ A(x-1)^\alpha + 1 & \text{for } x > 1, \end{cases} \quad (22)$$

where $A > 0$ and $\alpha > 1$. Note that the function $f(x)$ is continuous and differentiable everywhere.

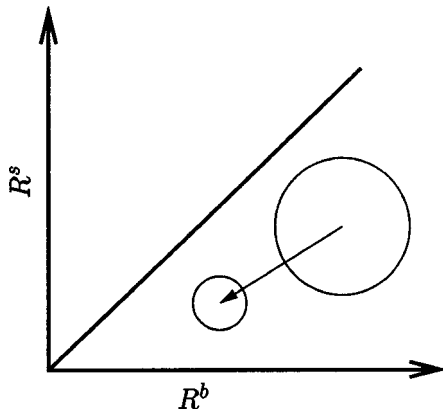


FIG. 1. Phase diagram for $R^* < R_m^*$. The 45° line is $R^b = R^s$. Arrow shows the direction of the air flux. The big balloon always inflates the smaller one.

Transfer of dn moles of air from the bigger balloon to the smaller one will occur spontaneously if the pressure inside the bigger balloon is larger than the pressure inside the smaller balloon. To simplify the notation, let us measure all the lengths in units of R_0 and define $R^s = uR^b$ with $\{1/R^b \leq u \leq 1\}$. Using the law of Laplace,

$$g(u; R^b, R^*, A) \equiv P_b - P_s = \frac{2\sigma(R^b)}{R^b} - \frac{2\sigma(uR^b)}{uR^b}. \quad (23)$$

If $g > 0$, once the valve is open there will be a spontaneous transfer of gas from the larger balloon to the smaller one. On the other hand, if $g < 0$ the transfer will proceed in the opposite direction. From Eqs. (21) and (22) we see that $g(1; R^b, R^*, A) = 0$ while

$$\lim_{u \rightarrow 1/R^b} g(u; R^b, R^*, A) = \frac{2\sigma(R^b)}{R^b} > 0. \quad (24)$$

Therefore, unless the function g has a zero on the interval $\{1/R^b \leq u \leq 1\}$ the larger balloon will always shrink, passing its air to the smaller balloon. Indeed for a given $f(x)$, we find

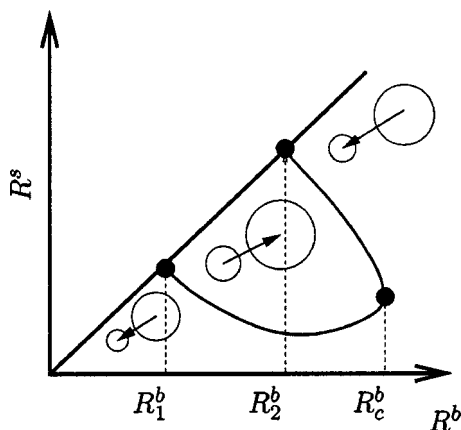


FIG. 2. Phase diagrams for $R^* > R_m^*$. There are two distinct regimes, separated by a phase boundary terminating at a critical point, beyond which a large balloon will inflate any smaller balloon.

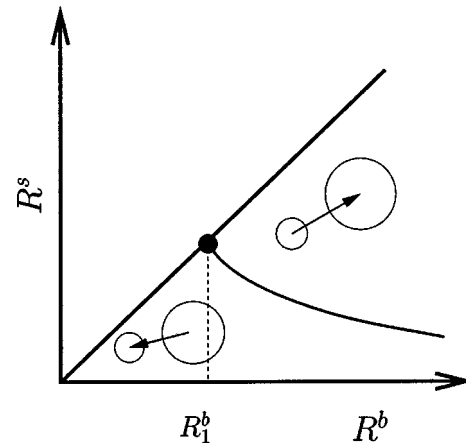


FIG. 3. Phase diagram for the ideal rubber balloons, $R^* \rightarrow \infty$.

that if $R^* < R_m^*$ then $g > 0$ for all $\{1/R^b \leq u \leq 1\}$, and the larger balloon always inflates the smaller one, see Fig. 1. The maximum value of the crossover scale R_m^* and the balloon size R_m^b for which this behavior occurs is determined by the set of equations

$$g'(1; R_m^b, R_m^*, A) = 0 \quad (25)$$

and

$$g''(1; R_m^b, R_m^*, A) = 0, \quad (26)$$

where the prime denotes differentiation with respect to u .

We now distinguish two cases: $1 < \alpha < 2$ and $\alpha \geq 2$. For $\alpha \geq 2$ and $R^* > R_m^*$, the equation

$$g'(1; R^b, R^*, A) = 0 \quad (27)$$

has two roots R_1^b and R_2^b and a new phase in which small balloons inflate the larger ones appears, see Fig. 2. This phase terminates at a critical point, beyond which a large balloon with size $R^b > R_c^b$ will inflate any smaller balloon. For a given crossover function and crossover scale R^* , the

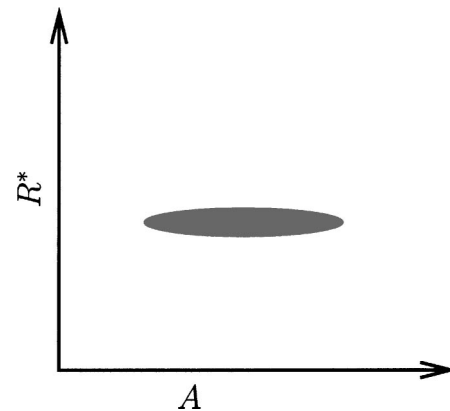


FIG. 4. The shaded region indicates the parameters for which the topology of the phase diagram is the one shown in Figs. 5 and 6. Outside the shaded region the topology is the one presented in Figs. 1–3. As $\alpha \rightarrow 2$ the shaded area shrinks to zero.

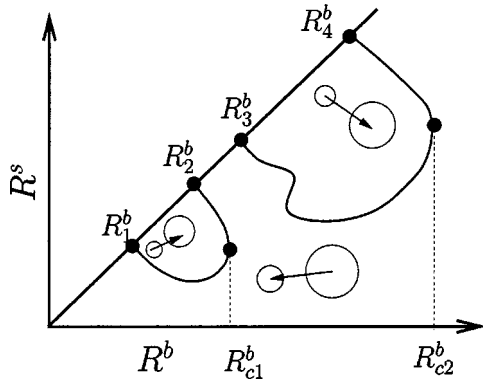


FIG. 5. Possible phase diagram for $1 < \alpha < 2$. As $R_3^b \rightarrow R_{c1}^b$ there is a topological change with the new phase diagram shown in Fig. 6.

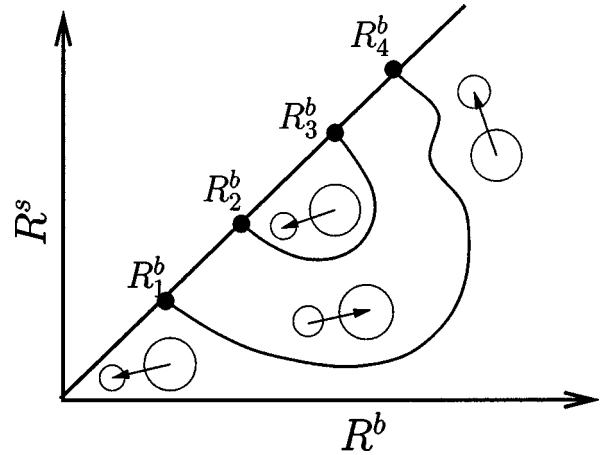


FIG. 6. Possible phase diagram for $1 < \alpha < 2$.

location of the critical point is determined by the set of equations

$$g(u_c; R_c^b, R^*, A) = 0, \quad (28)$$

and

$$g'(u_c; R_c^b, R^*, A) = 0. \quad (29)$$

As the crossover scale grows, so do the values of R_2^b and R_c^b . For $R^* > 1$,

$$R_2^b \approx aR^*, \quad (30)$$

where a is the root of equation,

$$a = \frac{A(a-1)^\alpha + 1}{A\alpha(a-1)^{\alpha-1}}. \quad (31)$$

If the crossover scale goes to infinity, $R^* \rightarrow \infty$, so that balloon rubber always behaves ideally, then $R_2^b \rightarrow \infty$ and $R_c^b \rightarrow \infty$. In this limit the phase diagram assumes the topology presented in Fig. 3.

For $1 < \alpha < 2$, the phase diagram becomes even more interesting. For A and R^* inside the shaded area of Fig. 4, Eq. (27) has four solutions R_1^b, R_2^b, R_3^b , and R_4^b , and the possible topologies of the phase diagram are shown in Figs. 5 and 6. As the boundary of the shaded region is approached from

inside, one of the phases shrinks and disappears and the phase diagram assumes the topology of Fig. 2. Outside the shaded region, the only possible topologies are the ones presented in Figs. 1–3.

The topological change from Fig. 5 to Fig. 6 occurs as $R_3^b \rightarrow R_{c1}^b$. As $\alpha \rightarrow 2$, the shaded area in Fig. 4 shrinks to zero and the topology of the phase diagram reduces to the one presented in Fig. 2.

IV. CONCLUSION

We have explored the thermodynamics of air transfer between two partially inflated rubber balloons. Surprisingly, for such an apparently simple system a very rich phase diagram governing the air transfer between the two balloons is obtained. We find that depending on the elasticity of balloon rubber and the initial balloon sizes, the air can flow either from the larger balloon to the smaller one, or vice versa. The topology of the phase diagram is controlled by the crossover function which characterizes the deviation of balloon rubber from the ideal Flory behavior.

ACKNOWLEDGMENTS

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